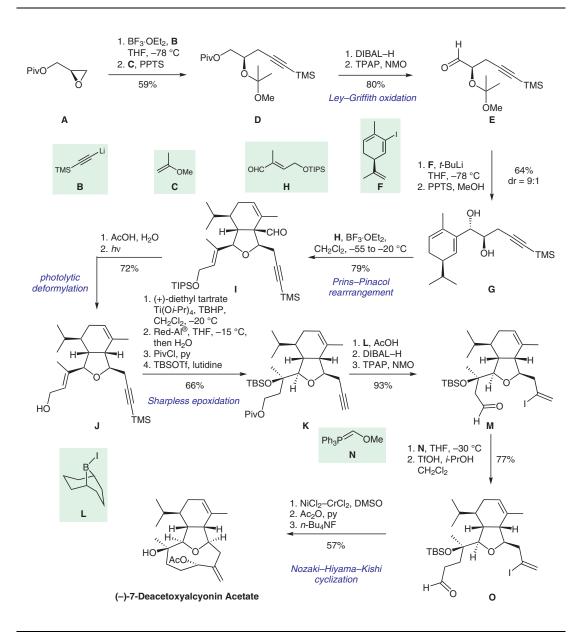
D. W. C. MACMILLAN, L. E. OVERMAN\* (UNIVERSITY OF CALIFORNIA, IRVINE, USA) Enantioselective Total Synthesis of (–)-7-Deacetoxyalcyonin Acetate. First Synthesis of a Eunicellin Diterpene *J. Am. Chem. Soc.* **1995**, *117*, 10391–10392.

## Synthesis of (–)-7-Deacetoxyalcyonin Acetate



**Significance:** The eunicellin diterpenes feature a synthetically challenging tricyclic ring system, including a hydroisobenzofuran and oxonane subunit. MacMillan and Overman reported in 1995 the first synthesis of a member of this natural product family in asymmetric fashion, confirming the relative and absolute configuration proposed by the isolation team. Highlights of this synthesis include use of a Prins–pinacol rearrangement to access the hydroisobenzofuran core as well as a photolytic deformylation of a  $\beta$ , $\gamma$ -desaturated aldehyde.

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Comment: The synthesis commences with regioselective opening of **A**, which was converted into aldehyde **E** in three steps. Dienyl iodide **F** was accessed in three steps starting with (*S*)-carvone. Fusing the two fragments set the stage for Prinspinacol rearrangement, affording **I** as a single stereoisomer. Deprotection and photolytic deformylation afforded intermediate **J**. The final oxonane ring was constructed using Nozaki–Hiyama–Kishi coupling, the natural product in two additional steps.

## Category

Synthesis of Natural Products and Potential Drugs

## Key words

eunicellin diterpenes

Prins-pinacol rearrangement

photolytic deformylation

Nozaki-Hiyama-Kishi reaction

